Raman Spectra of Diethyl Aluminum Monohalogenides

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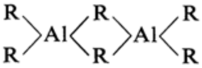
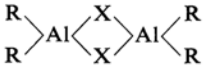
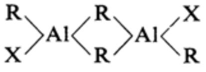
It has been established that some lower members of trialkyl aluminum have the molecular structure of the dimeric bridged form represented by



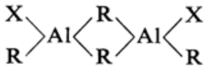
in which the plane containing two terminal alkyl groups and an aluminum atom is perpendicular to the bridge plane[1,2]. These compounds have been defined as " electron deficient compounds ", and according to Rundle[3] the bondings between the aluminum and bridging alkyl groups are formed by two " half bonds ". Monohalogen derivatives of trialkyl aluminum also exist as dimers, and the following structural formulae can be considered for them.



(A)



(B_1)



(B_2)

Formula A with symmetry D_{2h} has a halogen bridge which would be formed by the coordination of lone pair electrons in halogen atoms to aluminum. Formula B_1 with symmetry C_{2h} corresponds to the " trans " form, in which two halogen atoms are present on opposite sides of the bridge plane, while formula B_2 with symmetry C_{2v} corresponds to the " cis " form where the halogen atoms are on the same side of the bridge plane. In the latter two, the alkyl bridge would be formed by the half bonds, as in the case of trimethyl aluminum.

There have been several papers reporting on the structure of dimethyl aluminum monohalogenides. Van der Kelen and Herman[4] suggested after a study of the Raman spectra, that these compounds would have the structure B_2, while Growenewege proposed structure A for dimethyl aluminum chloride as a result of Raman[5] and proton nuclear magnetic resonance spectroscopy[6]. Electron diffraction study[7] by Brockway and Davidson also indicated that the compound would have the structure A. Recently Hoffmann[8] reported Raman and infrared spectral data on some members of trialkyl aluminum and dimethyl and diethyl aluminum chlorides, but his work was mainly concerned with CH deformations and little consideration was given to the structure of the diethyl aluminum monohalogenides.

In this paper, the Raman spectra of diethyl aluminum monohalogenides (except fluoride) as well as of triethyl aluminum have been reached from these spectra as to the structure studied, and some conclusions have been of diethyl aluminum monohalogenides.

Experimental

Materials.—All the materials except diethyl aluminum chloride were prepared by Gross and Mavity's methods[9]; diethyl aluminum bromide and iodide were prepared by the reduction of corresponding aluminum sesquihalides with sodium. Diethyl aluminum chloride was provided by the Meguro Laboratory of Mitsui Chemical Industry Co., Ltd. All the samples were distilled into Raman tubes, which were sealed off under reduced pressure to prevent contamination with air and moisture.

Raman Spectra.—The Raman spectra were obtained with a Cary 81 spectrophotometer. Qualitative polarization factor measurements were also made for the purpose of the tentative assignments.

Results and Discussion

The results are shown in Table I. It can be found from this table that the Raman lines are divided into three groups: 0~700 cm^{-1}, 900~1500 cm^{-1}, and 2700~3000 cm^{-1}, which represent skeletal vibrations, CH deformation vibrations and CH stretching vibrations respectively.

Of these three kinds of vibrations, the CH deformations and stretching vibrations are not so important as far as the molecular structure

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1) K. W. F. Kohlrausch und J. Wagner, *Z. physik. Chem.*, **B52**, 185 (1942).

2) P. H. Lewis and R. E. Rundle, *J. Chem. Phys.*, **21**, 986 (1953).

3) R. E. Rundle, ibid., **17**, 671 (1949).

4) C. P. Van der Kelen and M. A. Herman, *Bull. soc. chim. Belges*, **65**, 362 (1956).

5) M. P. Growenewege, *Z. physik. Chem.*, [*N. F.*], **18**, 147 (1958).

6) M. P. Growenewege, J. Smidt and H. de Vries, *J. Am. Chem. Soc.*, **82**, 4425 (1960).

7) L. O. Brockway and N. R. Davidson, ibid., **63**, 3287 (1941).

8) E. G. Hoffmann, *Z. Elektrochem.*, **64**, 616 (1960).

9) A. V. Gross and J. M. Mavity, *J. Org. Chem.*, **5**, 106 (1940).

TABLE I. RAMAN SPECTRA OF TRIETHYL ALUMINUM AND DIETHYL ALUMINUM MONOHALOGENIDES

$[Al(C_2H_5)_3]_2$		$[Al(C_2H_5)_2Cl]_2$		$[Al(C_2H_5)_2Br]_2$		$[Al(C_2H_5)_2I]_2$	
$\Delta\nu$, cm^{-1}	I	$\Delta\nu$, cm^{-1}	I	$\Delta\nu$, cm^{-1}	I	$\Delta\nu$, cm^{-1}	I
119	30 dp	114	44 dp	95	66 dp	81	100 dp
196	sh dp	164	3 dp	183	sh dp	170	85 p
269	91 dp	239	27 dp	197	100 p	202	25 p
362	18 p	263	19 p	236	11 dp	268	20 p
430	100 p	339	56 p	266	26 p	321	25 p
560	66 p	480	5 p	319	23 p	544	100 p
640	30 dp	556	100 p	547	100 p	664	34 dp
		670	27 dp	664	27 dp		
922	8 dp	922	5 dp	921	3 dp	921	3 p
955	12 p	957	10 p	954	12 p	956	8 p
979	41 dp	990	45 dp	988	24 dp	987	19 dp
1190	62 p	1107	1 p	1074	3 p	1098	3 p
1384	1 dp	1197	74 p	1132	3 p	1132	3 p
1404	19 dp	1379	1 dp	1190	84 p	1189	154 p
1460	36 dp	1406	23 dp	1377	2 dp	1381	5 dp
		1463	46 dp	1402	15 dp	1404	11 dp
				1459	25 dp	1462	22 dp
2724	9 p	2732	17 p	2733	8 p	2731	6 p
2792	18 p	2786	14 p	2789	22 p	2790	24 p
2827	54 p	2870	420 p	2866	300 p	2867	360 p
2864	565 p	2904	115 dp	2900	73 dp	2901	33 dp
2896	153 dp	2943	230 dp	2939	160 dp	2940	78 dp
2938	260 dp						

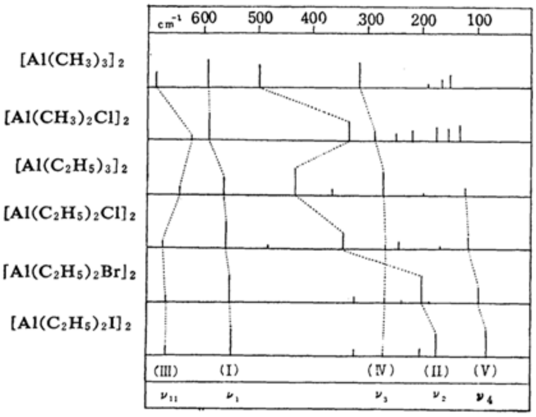

Fig. 1. Schematic representation of Raman spectra in 0∼700 cm^{-1} region of diethyl aluminum halogenides and related compounds.

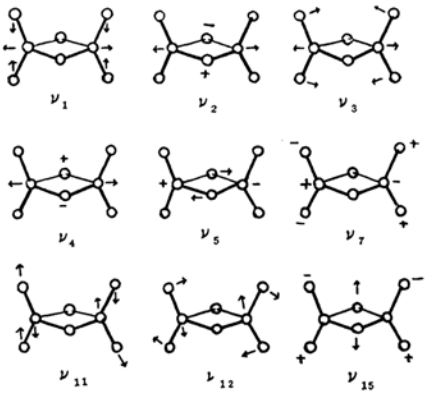

Fig. 2. Normal modes of Raman active vibrations of A_2B_6 type molecule.
ν_1, outer stretching; ν_2, bridge stretching; ν_3, outer bending; ν_4, bridge bending; ν_6, bridge stretching; ν_7, outer wagging; ν_{11}, outer stretching; ν_{12}, outer rocking; ν_{15}, outer twisting.

is concerned. Furthermore, the CH deformations were discussed in some detail by Hoffmann8), and it appears that there is nothing to be added to his paper. Therefore, the author was interested mainly in the skeletal vibrations and left the CH stretching vibrations to be assigned in the near future.

Tentative assignments for the skeletal vibrations were obtained by comparison with the known spectra of aluminum trihalogenides10,11), trimethyl aluminum1), and dimethyl aluminum chloride5), for which the bridged structure has been firmly established by many authors. The skeletal vibration lines

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10) R. P. Bell and H. C. Longuest-Higgins, *Proc. Roy. Soc.*, A183, 357 (1945).

11) W. Klemperer, *J. Chem. Phys.*, **24**, 353 (1956).

obtained of the compounds in question are schematically drawn in Fig. 1, in which the notation for the frequencies of Bell and Longuet-Higgins10) is used. The modes of vibrations of A_2B_6 type molecules are reproduced in Fig. 2 only for Raman active vibrations, symmetry species and polarization characters of which are shown in Table II.

TABLE II. SYMMETRY SPECIES AND POLARIZATION CHARACTERS OF THE RAMAN ACTIVE NORMAL VIBRATIONS IN Fig. 2

D_{2h}	A_{1g} (p)	ν_1, ν_2, ν_3, ν_4
	B_{1g} (dp)	ν_6, ν_7
	B_{2g} (dp)	ν_{11}, ν_{12}
	B_{3g} (dp)	ν_{15}

Seven to eight Raman lines are observed in the region of the skeletal vibrations of the monohalogenides. In the case of the C_{2h} symmetry model, structure B_2, all of the 18 possible skeletal vibrations are Raman active, while only nine of the vibrations are Raman active for the D_{2h} or C_{2h} symmetry model. It is probable, therefore, that diethyl aluminum monohalogenide has a D_{2h} or C_{2h} symmetry, although this does not appear to be conclusive. Futhermore, in the 400～700 cm^{-1} region of diethly aluminum chloride four infrared absorption bands were observed8), at 673, 628, 544 and 438 cm^{-1}, which, except for 673 cm^{-1}, do not accord with the Raman lines in Table I. If 673 cm^{-1} in the infrared and 670 cm^{-1} in the Raman spectra can be assigned to each different vibration, and if it is noted that no other infrared band agrees with any of the Raman lines in frequency, it can be considered that the rule of mutual exclusion holds; this fact assures the presence of the center of symmetry in the molecule. Unfortunately, there is no infrared data on diethyl aluminum monobromide and iodide, but the possibility of C_{2v} symmetry can be eliminated with considerable certainty.

In the Raman spectra of trietyl aluminum and diethyl aluminum monohalogenides the following two series of strong lines are observed:

X of $[Al(C_2H_5)_2X]_2$	Series I cm^{-1}	Series II cm^{-1}
Et	560	430
Cl	556	339
Br	547	197
I	544	170

Since both series of lines are polarized, these must be either ν_1, ν_2, ν_3, or ν_4 for D_{2h} symmetry. Furthermore, it is reasonable to assume that series I and II are assigned to either ν_1 or ν_2 by comparison with the assignment of the spectrum of trimethyl aluminum.

Now if the halogen bridge model A with symmetry D_{2h} is acceptable, series II must be assigned to ν_2, the bridge stretching vibration, because it varies in frequency with the increase in the atomic weight of substituents while series I does not. The frequencies of the bridge stretching vibration, ν_2, of aluminum trihalogenides are 340, 204 and 146 cm^{-1} for chloride, bromide and iodide respectively, as is shown in Table III, in which the Raman lines in the skeletal regions of trimethyl aluminum, dimethyl aluminum chloride and aluminum trihalogenides are listed with the normal vibrations to which they are assigned. Thus, it can be found that there is a close relationship in ν_2 between the trihalogenides and diethyl aluminum monohalogenides. When series II is assigned to ν_2, series I is naturally assigned to ν_1, the outer stretching vibration.

If the halogen bridge model A is assumed, the remaining outer vibrations ν_3, ν_7, ν_{11} and ν_{12} must not vary in frequency with the increase in the atomic weight of the substituents. Thus, the series III, 640(Et), 670(Cl), 664(Br) and 664(I) cm^{-1} is assigned to the outer stretching vibration ν_{11} by comparison with methyl compounds and by a consideration of polarization factors. Series IV, 269(Et), 263(Cl), 266(Br) and 268(I) cm^{-} may be assigned to the outer bending vibration ν_3. The depolarized series V, 119(Et), 114(Cl),

TABLE III. RAMAN LINES IN THE REGION OF 0～700 cm^{-1} OF TRIMETHYL ALUMINUM, DIMETHYL ALUMINUM CHLORIDE AND ALUMINUM TRIHALOGENIDES

	$[Al(CH_3)_3]_2$1)	$[Al(CH_3)_2Cl]_2$5)	$Al_2Cl_6$10)	$Al_2Cl_6$11)	$Al_2Br_6$10)	$Al_2I_6$10)
ν_1	590 (10 p)	588 (10)	606 ($2^1/_2$ p)	506	491 (3)	406 (3)
ν_2	452 (8 p)	332 (7)	340 (10 p)	340	204 (10)	146 (10)
ν_3	314 (9 p)	286 (4)	217 (5 p)	217	140 (5)	94 (6)
ν_4	148 (5)	131 (6)	112 (6 dp ?)	112	73 (6)	53 (6)
ν_{11}	682 (5 dp)	620 (2)	506 (3 p)	606	407 (2)	344 ($2^1/_2$)
ν_{12}	188 (1)	173 (5)	164 (3 dp)	164	112 (3)	—
ν_6	563 (00)	247 (3)	438 ($^1/_2$ dp ?)	438	(291 ?)	(195 ?)
ν_7	164 (3)	152 (5)	284 (2 dp)	164	176 (2)	—
ν_{15}	—	217 (4)	—	(160)	—	—

95(Br), and 81(I) cm^{-1} might be ν_4 by intensity consideration, although ν_4 has to be a polarized vibration.

So far the assignments have been performed with the halogen bridge model. If the alkyl bridge model, B_1 with symmetry C_{2h} (trans form), is adopted, series which does not vary in frequency is the bridge vibration, so that polarized series I should be a bridge vibration. But even in this case triethyl aluminum must belong to the same symmetry class D_{2h} as trimethyl aluminum, so that, for example, 560 cm^{-1} of triethyl aluminum in series I should be assigned to ν_1, the outer vibration, by comparison with ν_1 and ν_2 of trimethyl aluminum. With the model B, all of the monohalogenides have the alkyl bridge. Then strong lines at approximately 430 cm^{-1} should also be observed as the bridge stretching vibration in the spectra of the monohalogenides as in the case of triethyl aluminum. Actually it is not the case, however. Furthermore, it is impossible to interpret the marked correlation of frequencies between the triethyl aluminum and the diethyl aluminum monohalogenides obtained in Table I.

Accordingly, the results of this study indicate that the Raman spectra of diethyl aluminum chloride, bromide and iodide are consistent with a dimeric bridge structure over the halogen atoms with symmetry D_{2h}.

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